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MEASUREMENTS OF PARTICLE FORMATION IN FLAMES INHIBITED BY IRON PENTACARBONYL*

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Certain metallic compounds have been found to be substantially more effective flame inhibitors than halogen-containing compounds [1-3]. In particular, iron pentacarbonyl ($Fe(CO)_5$) was found to be one of the strongest inhibitors—up to two orders of magnitude more effective than CF_3Br at reducing the burning velocity of premixed hydrocarbon-air flames [1,4]. Although $Fe(CO)_5$ is highly toxic, understanding its inhibitory effect could lead to development of effective non-toxic agents.

Measurements of $Fe(CO)_5$-inhibited premixed flames [5] have shown that the inhibition varies with the $Fe(CO)_5$ concentration: at low mole fraction the burning velocity is strongly dependent on inhibitor mole fraction, while at high $Fe(CO)_5$ mole fraction the burning velocity is nearly independent of inhibitor mole fraction. A critical part of the research on $Fe(CO)_5$ is to understand iron pentacarbonyl's diminishing effectiveness at high mole fraction in order to avoid similar behavior in future fire suppressants. A plausible but unconfirmed explanation for iron pentacarbonyl's reduced effectiveness under certain conditions is that particles form, thus reducing the gas-phase mole fraction of active inhibiting species [5]. To investigate this possibility, we use laser-light scattering to measure particles in premixed flames with added $Fe(CO)_5$ and determine if the conditions of high particle concentration correspond to the regions of reduced inhibition effect. Alternatively, if there is high particle density for conditions at which $Fe(CO)_5$ has a strong inhibition effect, then the search for halon alternatives could be directed toward chemicals that produce similar condensed-phase compounds.

EXPERIMENTAL

The premixed burner system has been described in detail in previous papers [5]. Premixed flames are stabilized on a Mache-Hebra nozzle burner (inner diameter 1.02 ± 0.005 cm), without a shroud flow around the burner. Figure 1 shows a schematic of the flame geometry as well as the location of the scattering measurements. The total area method is used to measure the laminar burning velocity of flames with various amounts of $Fe(CO)_5$ added. The reduction in burning velocity is a measure of the inhibition effect of $Fe(CO)_5$.

Gas flows are controlled with digitally-controlled mass flow controllers. The fuel gas is methane, and the oxidizer stream consists of nitrogen and oxygen. Inhibitor is added to the flame by diverting part of the nitrogen stream to a two-stage saturator, where it bubbles through liquid $Fe(CO)_5$ before returning to the main nitrogen flow. The burner is mounted on a three-axis translation stage (minimum step size of 0.0016 mm).

We use laser-light scattering with phase-sensitive detection to determine particle density and location. The apparatus is similar to those used by other researchers [6,7]. The light source is an 4-W argon-ion laser, with a vertically polarized beam at 488 nm. Variations in laser power during the experiment are measured by a reference detector. The detection system for light scattered normal to the laser beam consists of a circular aperture, collection lens, pinhole aperture, laser-line filter, polarizer and 1P28 photomultiplier tube. A personal computer controls the amplifiers and records the

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measurements during the experiments. In the data acquisition software, each scattering data point is normalized by the reference signal to account for variations in laser power. Typically, 500 readings are averaged over a time of about 1 second. After data collection is complete, the magnitude of the scattering signals are adjusted so that a signal of unity corresponds to scattering from room temperature air. Measurements are made in flames at the same conditions as the original inhibition measurements described in Ref. [5].

Uncertainties are reported as *expanded relative uncertainties*: $X \pm U / X \cdot 100\%$, where U is ku_c, and is determined from a combined standard uncertainty (estimated standard deviation) u_c, and a coverage factor $k = 2$ (level of confidence approximately 95%). Details about the uncertainty analysis can be found elsewhere [8]. The uncertainty of normalized burning velocity measurement is between 1 and 3% and the overall uncertainty of $Fe(CO)_5$ mole fraction is approximately 6.5%. For the scattering measurement, the combination of instability in the flame, the small particle scattering cross section, and system noise cause the scattering signal to vary at any given location. The maximum standard deviation is no more than 2% of the mean in the reaction zone and in the unburned reactants, and no more than 10% of the mean outside of the main reaction zone.

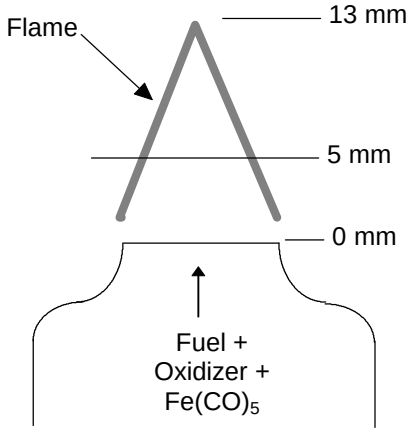

Figure 1: Schematic of premixed flame, showing the dimensions of the flame. The horizontal line at 5 mm denotes the location of the measurements. The inner diameter of the burner tube is 1.02 cm.

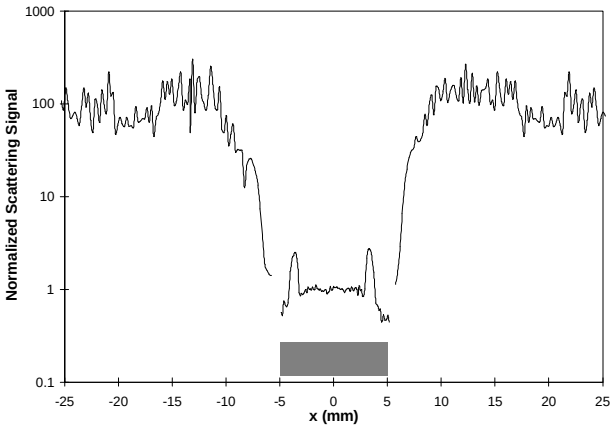

Figure 2: Scattering at 5 mm height in ϕ=1.1 CH_4-air flame with 300 ppm of $Fe(CO)_5$. The inner curve was obtained using high amplifier sensitivity; the outer curves were obtained using low sensitivity. The grey rectangle marks the location of the burner exit.

RESULTS AND DISCUSSION

The nozzle burner readily provides burning velocity data over a range of conditions and is amenable to modeling. Addition of iron pentacarbonyl leads to a very interesting two zone structure for particle formation, which, unfortunately, makes extinction measurements difficult for this burner type. Figure 2 provides an overview of the gross features of the particles in a premixed CH_4-air flame with 300 ppm of $Fe(CO)_5$ and ϕ=1.1. In Figure 2, the inner (-5 mm < r < 5 mm), lower curve was obtained using high amplifier sensitivity, and the outer (-25 mm < r < 25 mm) curve was obtained using low sensitivity. Particles form in the main reaction zone of the flame, yielding a peak scattering signal a few times higher than that from Rayleigh scattering from the cold reactants. These particles disappear outside the main reaction zone of the flame, and far downstream, very large or numerous particles form with a scattering signal about 100 times that of the cold reactants. Note that the small *scattering* signal in the flame zone can be accurately measured by carefully positioning the flame relative to the optics, and properly adjusting the sensitivities of the lock-in amplifiers. It is much more difficult, however, to determine the extinction caused by the particles in the inner premixed flame zone along the line of

sight at a height of 5 mm. The magnitude of the extinction (less than 1%) and the disparate scattering signal strengths in the two regions of the flame make tomographic reconstruction impractical. Nonetheless, in the absence of extinction data (and the resulting particle size and number density information) we can still use the scattering data to study particulate formation in the premixed flames.

In order to determine how particle formation depends on $Fe(CO)_5$ concentration, we measured radial profiles of the scattering for varying amounts of $Fe(CO)_5$ (Figure 3). The measurements were made at a height of 5 mm above the burner, with a radial step size of 0.1 mm. Starting at r = 0 and moving outward, reactants are in the region of $|r| < 2$ mm, the primary reaction zone of the flame extends from $|r| \sim 2$ to 3 mm, and the hot combustion products are in the region of $|r| > 3$. The figure shows that at 100 ppm, the scattering signal is nearly equivalent to that of the uninhibited flame, but above that value, significant peaks in scattering signal appear in the flame zone, indicating particle formation. The existence of sharp peaks in Figure 3, as opposed to a step function, may be explained as follows: in the reaction zone ($|r| > 2$), the $Fe(CO)_5$ decomposes, resulting in supersaturated vapor of iron-containing intermediates (which are believed to be the inhibiting species). If the mole fraction of these species is high enough, nucleation and particle growth occurs. As the particles are heated by the flame ($|r| > 3.25$), they evaporate, thus reducing the scattering signal.

Evidence that particle formation leads to the decrease in effectiveness described in Ref. [5] is found in Figure 4, which shows the scattering signal due solely to particles along with the normalized burning velocity for various inhibitor concentrations. The maximum particle scattering is calculated by finding the maximum difference in scattering between the inhibited and uninhibited flame. In regions where the normalized burning velocity depends strongly on $Fe(CO)_5$ concentration, the particle signal is relatively small (<200 ppm), but as the marginal effect of the $Fe(CO)_5$ decreases to nearly zero (>200 ppm), the particle signal rises sharply.

There have been conflicting claims in the literature as to whether inhibition by $Fe(CO)_5$ is a gas-phase or heterogeneous effect [1,4,9-11]. The strong correspondence between rate of change of the normalized burning velocity and the maximum particle scattering (Figure 4) suggests that the inhibition is primarily gas-phase. If the inhibition chemistry were heterogeneous, we would expect the maximum particle scattering to be high for $Fe(CO)_5$ mole fraction below 200 ppm, and leveling-off above 200 ppm. Information about the relationship between $Fe(CO)_5$ concentration and particle surface area would help to improve understanding of the relative importance of gas-phase and heterogeneous chemistry.

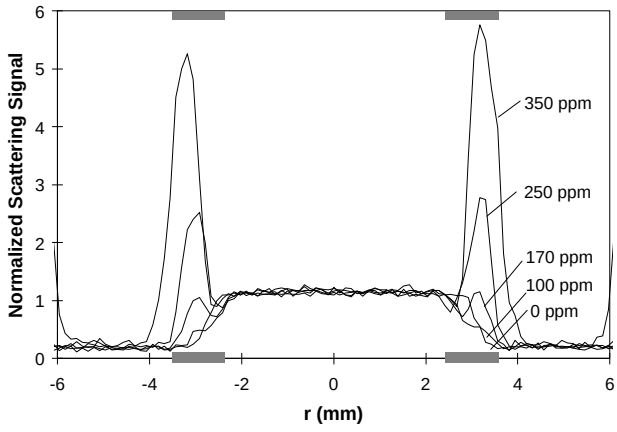

Figure 3: Normalized scattering signal through a ϕ=1.1 CH_4-air flame 5 mm above the burner rim. The grey bars at top and bottom roughly mark the flame zone.

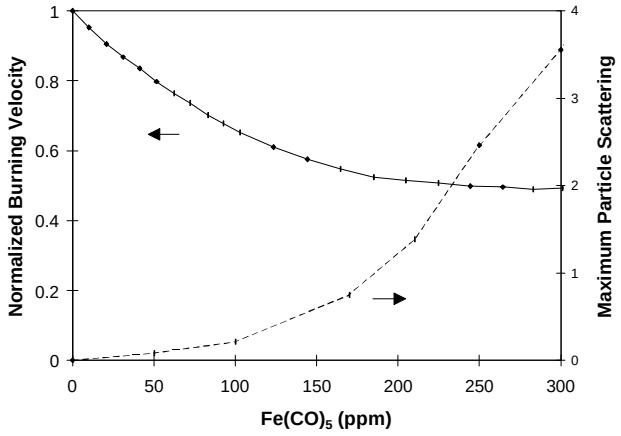

Figure 4: Normalized burning velocity and maximum particle scattering for ϕ=1.1 CH_4-air flame. Data from Ref. [5].

CONCLUSION

Laser light scattering has been used to investigate particle formation in $Fe(CO)_5$-inhibited premixed flames. Particles form early in the flame zone, reach a peak, then disappear as the temperature increases to the flame temperature. The $Fe(CO)_5$ mole fraction at which particle formation begins to sharply increase corresponds to the point at which the normalized burning velocity levels-off, thus supporting the hypothesis that condensation reduces the inhibition effect. Additionally, the measurements support the hypothesis that inhibition is primarily a gas-phases effect. Further measurements of particle size and morphology using thermophoretic sampling and electron microscopy are needed to more conclusively determine the role of particles in $Fe(CO)_5$ inhibition.

The particle measurements described here provide insight into many of the questions about the behavior of $Fe(CO)_5$ in premixed flames. Future measurements will also address $Fe(CO)_5$ in counterflow diffusion flames. For counterflow diffusion flames of diluted fuel vs. O_2 enriched air, addition of $Fe(CO)_5$ to either the fuel or the oxidizer stream for some (but not all) of the flames result in little reduction in the measured extinction strain rate, whereas calculations of extinction strain rate using the mechanism in [11] show a significant decrease in extinction strain rate as the inhibitor concentration increased. Since the flames are cooler than the premixed flames it is possible that more particles are forming and removing a larger fraction of the inhibiting gas-phase species. Particle measurements could help explain the loss of effectiveness and the mechanism of inhibition (heterogeneous or gas-phase) for counterflow diffusion flames.

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